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## TIME FACTORS IN THE IONIZATION OF CARBON DISULPHIDE BY X-RAYS

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### ABSTRACT

The conductivity of  $\text{CS}_2$  exposed to X-rays varies with the time of application of voltage and time of exposure. It is shown that the various phenomena observed can be explained by barrier potentials due to space charge. Effects with X-rays appear to differ only in degree from those observed without X-rays. At direct-current fields of 70 kv/cm the conductivity had reached about 75 percent of its saturation value. Measurement of the barrier potential showed it to be linear with applied potential; to decrease with increase in radiation intensity; and to vary from 40 to 60 percent of the applied voltage. Current-decay curves obey a simple power law, the power of time changing very slowly with field strength within a given time interval. Square-wave voltage was applied to the cell and short interval current measurements made under essentially direct-current conditions. Current-decay curves for intervals as small as 0.004 sec follow out those made for longer times, but show a sharp increase at about 0.02 sec due probably to sweeping out the initial ions formed in a field-free cell.

Reciprocal plots of ionization current against voltage show the same linearity at high fields as reported previously. Such plots obtained with direct-current or square-wave voltage extrapolate to the same point for  $1/V=0$ , from which the saturation current may be derived. Using this method, saturation conditions were studied for several types of ionization chamber with different X-ray intensities and qualities. The application of this work to the problem of radiation measurements is discussed briefly, and, in a large measure, it verified our earlier work carried out in less detail.

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## I. INTRODUCTION

Various workers have studied the conductivity effect of ionizing radiations on highly insulating dielectric liquids. Among the earliest work was that of Jaffé<sup>1</sup> and his students,<sup>2</sup> who studied the effects of alpha rays and gamma rays on a number of liquids, including carbon disulphide, carbon tetrachloride, and hexane, and explained the current-voltage curves by the theory of columnar ionization.

There are definite dissimilarities between the ionization produced by X-rays in liquids and gases. In liquids the ions are concentrated in densely populated groups or columns within which the recombination rate is very high. As a result of this, the fields normally used to withdraw all the ions produced in a gas (200 v/cm), furnish a measured ionization current which, in liquids, is only a small fraction of the saturation current. Also, electrical breakdown of a strongly ionized liquid occurs at field strengths far below saturation current conditions. A further important difference is that various complicated time effects are involved in the ionization of liquids, so that the measured current depends upon the time lapsed after application of voltage and radiation. These time effects were first noted by Jaffé<sup>3</sup> for liquids exposed to radiation and later studied in considerable detail by Whitehead and Marvin<sup>4</sup> for transformer oils at moderate field strengths but not exposed to radiation. Recent tests of Jaffé's theory have been made by Mohler and Taylor,<sup>5,6</sup> Zanstra,<sup>7</sup> and Clay and van Tijn.<sup>8</sup> Also Stahel<sup>9</sup> has constructed very small ionization chambers with which he has investigated the distribution of intensity of gamma-ray ionization produced in water phantoms. His work being concerned only with relative intensity measurements, he used comparatively low field strengths.

Jaffé's theory leads to the following relationship for the ionization current  $I_x$  at any field  $X$ :

$$\frac{I_\infty}{I_x} = 1 + \frac{\alpha N}{7.85duXf(X)},$$

where  $\alpha$  is the recombination coefficient;  $u$  the ion mobility;  $N$ , the density of ion pairs per centimeter of column length; and  $d$ , the column diameter. Since  $f(X)$  is a complicated function, and not easily evaluated at the fields employed by Jaffé (5 kv/cm) this equation was not used to determine the saturation current. However,<sup>10</sup>  $f(X)$  approaches 1 for applied fields in excess of about  $10^4$  v/cm and a plot of  $1/I_x$  against  $1/X$  approaches a straight line which can be extrapolated to give the reciprocal of the current at infinite fields. This method was successfully employed in the determination of the number of ions per quantum absorbed for liquid carbon bisulphide.

<sup>1</sup> G. Jaffé, Ann. Physik **42**, 331 (1913); Le Radium **10**, 126 (1913).

<sup>2</sup> H. J. van der Bijl, Verhandl. deut. phys. Ges. **15**, 102 and 210 (1913).

<sup>3</sup> G. Jaffé, Ann. Physik **25**, 257 (1908).

<sup>4</sup> J. B. Whitehead and R. H. Marvin, Trans. Am. Inst. Elec. Engrs. **49**, 649 (1930).

<sup>5</sup> F. L. Mohler and L. S. Taylor, J. Research NBS **13**, 659 (1934) RP733; Phys. Rev. **45**, 762 (1934).

<sup>6</sup> L. S. Taylor and F. L. Mohler, Sci. **81**, 318 (1935).

<sup>7</sup> H. Zanstra, Physica **2**, 817 (1935).

<sup>8</sup> J. Clay and M. A. van Tijn, Physica **2**, 825 (1935).

<sup>9</sup> E. Stahel, Strahlentherapie **31**, 582 (1929).

<sup>10</sup> See footnote 5.

The function  $f(X)$  has also been evaluated by Zanstra<sup>11</sup> for gas under pressures ranging from 8 to 400 atmospheres.

There is further interest in the problem of ionization of liquids by radiation, from the point of view of its application to the comparison of X-ray and gamma-ray dosage in materials which approximate the physical properties of body tissue.<sup>12</sup>

In refining and extending the earlier measurements numerous interesting features developed, and it is the main purpose of this paper to discuss these features and their bearing upon the measurement of X-rays with liquid ionization chambers. Since the purpose of this work was to later apply the results practically, an endeavor was made throughout, to keep the technique as simple and inexpensive as possible.

## II. LIQUIDS

It was desired that the liquids used have the following properties: (1) Low conductivity when not exposed to ionizing radiation; (2) a relatively large increase in conductivity when exposed to ionizing radiations; (3) effective atomic number, about that of water (7.5); (4) low viscosity; (5) density of about 1; and (6) low volatility (preferred but not positively essential.)

Of the various liquids tested<sup>13</sup> carbon bisulphide, ligroin, and tetrahydronaphthalene (tetralin) were most suitable. While ligroin and tetralin, having effective atomic numbers of about 6, were found better suited to the problem of radiation measurement, they had the disadvantage of showing a relatively small increase in conductivity, compared with CS<sub>2</sub>, when exposed to X-rays. Consequently, CS<sub>2</sub> was used in the bulk of the exploratory work. It gave large ionization currents and was relatively easy to purify; however, the dark current was about 10 times that for ligroin and tetralin.

Some degree of purification of all the liquids was necessary and with CS<sub>2</sub> it was found that this could be attained without the more elaborate vacuum-distillation scheme used by us earlier.<sup>14</sup> Of primary importance was the removal of all traces of lint or dust suspended in the liquid. This necessitated all assembly and filling operations to be carried out within a dust-free hood.

In the early work, a reagent grade of CS<sub>2</sub> was passed about 10 times through the same filters of ordinary acid-free filter paper and thence into the ionization chamber. This process dried and cleaned the liquid with fairly satisfactory results. More recently, the CS<sub>2</sub> was refluxed with a reagent grade of P<sub>2</sub>O<sub>5</sub>, after which it was distilled directly into the cell. The cell was then placed under a bell jar which was thereupon exhausted to the point of producing mild boiling of the liquid, this serving to remove any gas bubbles or pockets. This method appeared to be at least as satisfactory as either vacuum distillation or refluxing with sodium.<sup>15</sup>

The lowest conductivity obtained with CS<sub>2</sub> was  $7 \times 10^{-16}$  mhos, and for tetralin,  $5 \times 10^{-17}$  mhos—measurements being made at 22 °C, with a field strength of 60 kv/cm on a 1-mm layer, at least 15 min after application of a steady voltage.

<sup>11</sup> See footnote 7.

<sup>12</sup> See footnote 6.

<sup>13</sup> We are indebted to Dr. E. Wickers of the Chemistry Division of this Bureau for his assistance in searching for suitable liquids.

<sup>14</sup> F. L. Mohler and L. S. Taylor, J. Research NBS **13**, 659 (1934), RP733.

<sup>15</sup> We are indebted to Dr. R. T. Leslie, Research Associate, representing the American Petroleum Institute at this Bureau, for his assistance in trying various modes of purification.

### III. IONIZATION CHAMBERS

The choice of ionization chamber was, in part, determined by the application of the problem to dosage measurement. In the first place, it was desired to measure the total number of ions per cubic centimeter produced in a layer not more than 1 mm thick at the surface of a liquid "phantom." Secondly, it was desired to keep as small as possible any corrections for absorption in or scattering from the ionization-chamber electrodes.

The two chambers shown in figures 1, 2, and 3 were used in most of the experiments. The chamber in figure 1 consists of a square fused-quartz plate with notches ground in the edges and about which two separate grids of 0.1-mm aluminum were woven. In the center is a hole 10 mm in diameter constituting, with the grids, the volume in which the ionization is measured. When used in this simple form in a broad X-ray beam there are relatively large stray ionization currents between the grids around the outside of the cell. Since these stray currents may not be proportional to the field strength, they should be eliminated in quantitative work; this was done somewhat crudely by means of mica and quartz shields mounted around the edges of the chamber.

In the chamber in figure 2, the electrodes were essentially embedded in a series of carefully ground fused-quartz rings, which in turn were

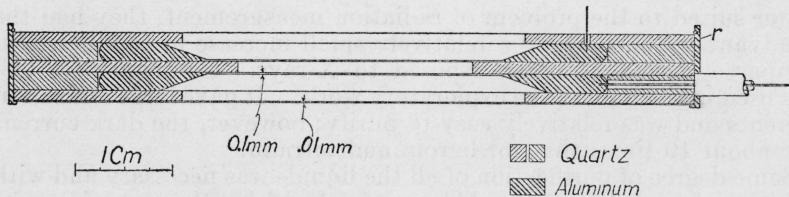


FIGURE 2.—Completely shielded cell.

held closely in position with a thin aluminum ring,  $r$ . The bottom of the cell was covered with 0.01-mm Al. The electrometer lead, supported on quartz beads, passed through a small aluminum tube which, together with the case, was grounded. It was thus impossible for any leakage current to reach the electrometer system except through the desired cell volume. The electrodes for this chamber could be either grids supported on perforated aluminum disks, figure 3, or solid aluminum disks. The latter were turned down at the center to a uniform thickness of about 0.1 mm and drilled with a number of 0.3-millimeter holes to facilitate removal of gas bubbles from the liquid. The use of undrilled plates was usually accompanied by unsteadiness of current at the higher field strengths because of small gas bubbles which could not escape.

The ionization chamber was placed in a shallow Pyrex dish of about 20-cc capacity. Leads extending through side tubes passed through grounded metal sleeves to avoid leakage. These tubes were plugged with tin, covered corks and sealed at the outer end with Duco cement. This cement was carefully tested in advance and found to be insoluble in the liquids used, as indicated by failure to affect the conductivity. Dried Cellophane cemented across the top of the dish made it satisfactorily airtight. The liquid to be used was

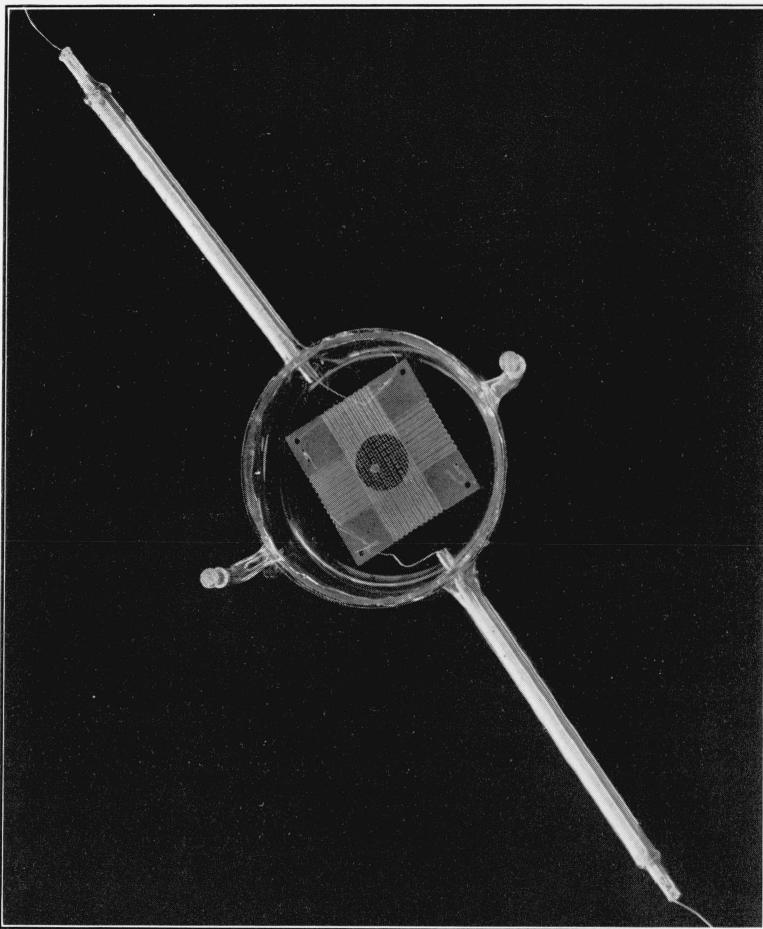


FIGURE 1.—*Square quartz-plate cell.*

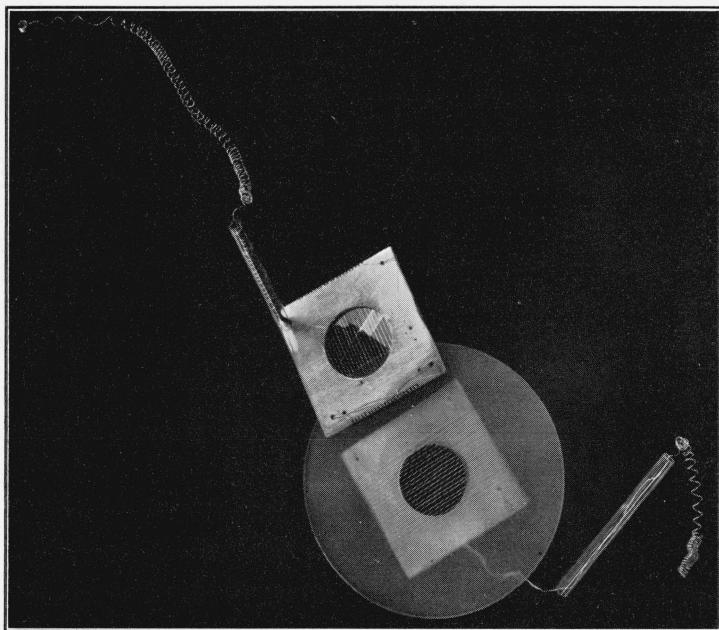


FIGURE 3.—*Aluminum electrodes for use in shielded cell.*

admitted through a short side tube after the whole assembly had been slowly baked for at least a day.

#### IV. RADIATION

X-rays of widely varying intensity and quality were produced by constant potential excitation in thick-walled air- or water-cooled tubes. The chamber was placed about 50 cm directly beneath the tube so that the beam passed through it normal to the plates. For comparison purposes the cell was used either imbedded in the surface of a large block of wax, or supported on a light cardboard platform essentially in free air. The X-ray beam was measured in roentgens per minute (r/min) by means of a calibrated thimble chamber.

#### V. IONIZATION CURRENT WITH DIRECT-CURRENT POTENTIAL

##### 1. CURRENT-VOLTAGE CURVES

The shape of the current-voltage curve with the ionization chamber exposed to X-rays was first investigated. It was observed in Jaffé's studies,<sup>16</sup> that the steady current value at a given applied potential was reached somewhat gradually, and that after removal of the radiation the return to zero was likewise slow after the first large initial drop. In our earlier work<sup>17</sup> readings were taken 2 minutes after the radiation or the applied voltage was changed.

Figure 4 shows the typical performance of an ionization chamber (grid or plate type) under different conditions, the current being plotted as a function of the time. With the first application of voltage, the current rises almost instantly to a maximum and then decreases to an essentially steady value in about 10 minutes. This is repeated after each *increase* of voltage; but when the voltage is *decreased* instead, the opposite occurs—the current starts at a low value and slowly rises to a final steady value. To obtain the same steady-state current after an increasing or decreasing voltage, a lapse of 20 to 30 min is required between the change in voltage and the measurement.

Just before each voltage change in figure 4, the X-rays were shut off for about a minute, during which a reading of the "leakage" current was obtained. This leakage current was found to increase steadily with the applied voltage.

At the termination of the experiment, the voltage was cut off and the cell momentarily grounded. Upon reconnecting to the galvanometer, without applied voltage, a relatively large reverse current which decayed slowly to zero was observed. This action is, under similar conditions, typical of the various cells and liquids used.

Whitehead and his coworkers<sup>18 19</sup> have obtained somewhat analogous results when transformer oils were subjected without X-rays to fairly high fields (10 kv/cm). He advanced the theory that the effects were due to large space charges made up of ion clusters which gave up their charges only very slowly because of the mutual shielding of an aggregate.

<sup>16</sup> G. Jaffé, Ann. Physik **25**, 257 (1908).

<sup>17</sup> F. L. Mohler and L. S. Taylor, J. Research NBS **13**, 659 (1934) RP733.

<sup>18</sup> J. B. Whitehead and R. H. Marvin, Trans. Am. Inst. Elec. Engrs. **49**, 649 (1930); **52**, 667 (1933).

<sup>19</sup> J. B. Whitehead and S. H. Shevky, Trans. Am. Inst. Elec. Engrs. **54**, 603 (1935).

As seen below, we have used his general ideas to explain the various phenomena encountered here, although for the present we will not

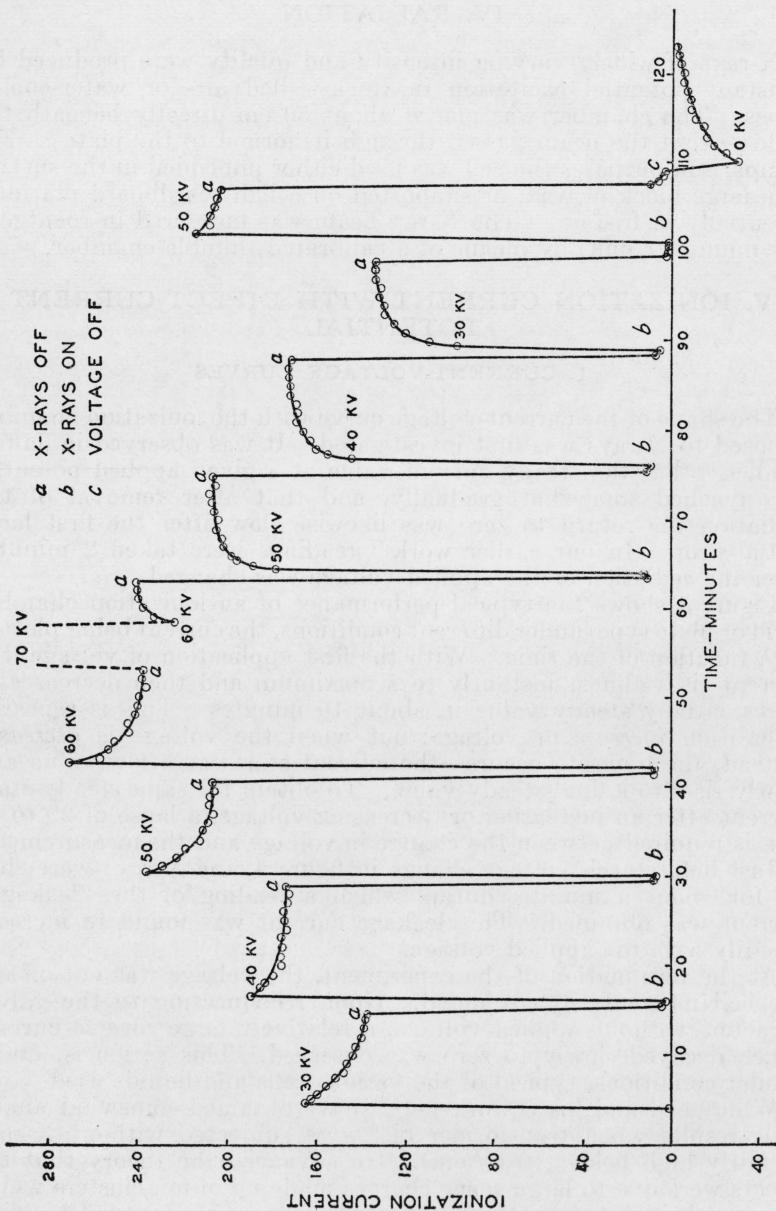


FIGURE 4.—*Current-time curves with different applied voltages.*

postulate either a space charge or other mechanism such as a polarized layer or barrier sheath at the electrodes.

In support of Whitehead's view we may outline very briefly some simple qualitative experiments with a cell filled with  $\text{CS}_2$  and connected as shown in figure 5.

A. With the X-rays off, a negative voltage ( $-V$ ) was applied to the plate  $a$ . The negative current to  $b$  had initially a high value  $i_1$ , then fell off, as indicated likewise in figure 4, to an essentially steady value in approximately 10 min. Such action may be explained by: (a) the building up of a negative space charge in the liquid or a negative sheath of bound charges at electrode  $a$ ; (b) the initial removal of a large fraction of the ions, which have accumulated in the field-free liquid before the voltage is applied, followed by a much smaller current representative of the rate of production of new ions.

B. After reaching a steady state, the voltage was removed and the cell electrodes momentarily earthed to remove any accumulated charge. On reconnecting the galvanometer, there was a small positive current,  $i_2 < i_1$ , to  $a$ , which decayed to zero in a few minutes. Assuming a space charge in the chamber, removal of the voltage essentially reverses the field within the cell and causes a current in the external circuit opposite in direction. If X-rays are applied to the chamber immediately after the removal of voltage, the positive current flow has a much higher initial value than the small one just mentioned, and appears to reach a steady dark-current state more quickly. Approximately the same quantity of electricity appears to flow in both cases—that is, the area under the time-current curves would be the same. The evidence of space charge is also checked by the charging (up to several hundred volts) of an electrometer connected to the cell after removing the voltage.

C. The unconnected chamber was first exposed to X-rays for some minutes, after which the X-rays were removed and voltage applied. In this case, a large initial negative current,  $i_3 \gg i_1$ , was soon followed by the usual decrease to a lower steady dark-current value. This was produced by an accumulation of ions in the field-free cell being cleared out to merely spontaneous-conduction conditions. The slow decay, rather than nearly instantaneous drop in current, could be ascribed to the building up of a space charge by the moving ions.

D. With X-rays on continuously, and the voltage changed in steps, the curves in figure 4 were obtained. They may be explained in the same way.

E. When using a grid-type chamber immersed in a large volume of liquid, the time required for the current to reach a steady state under any of the conditions noted, is about twice that required in the case of plate electrodes immersed in the minimum amount of liquid; but the end values of the current are the same. This might possibly be interpreted as indicating a volume distribution of space charge rather than a surface distribution, since it would be expected

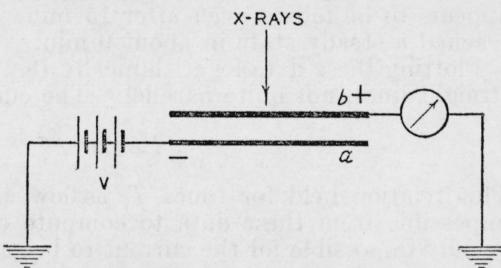


FIGURE 5.—Simple circuit arrangement of cell.

that the latter would be built up, independently of the amount of liquid which circulated between the plates.

## 2. FORM OF CURRENT-TIME CURVES

It is obvious from the preceding that "conductivity" has little significance without specifying the time lapsed between the application of voltage and measurement of the conductivity. For the purposes of our study, it is also necessary to know the effective field within the chamber. We accordingly investigated the form of the direct-current current-time curves.

For measurements at intervals greater than a minute, a short-period galvanometer was used; for shorter intervals, a string electrometer, with a period less than 0.005 sec measured the potential drop over a resistor of about  $10^9$  ohms (S.S. White). Transit times past the scale divisions were observed visually and recorded on a chronograph tape; longer intervals were timed with a split-second stopwatch.

Figure 6 shows two current-time curves obtained with a 1-mm grid ionization chamber exposed to X-rays and having applied voltages of 20 kv and 40 kv/cm, respectively. The 20-kilovolt curve appears to be falling even after 15 min, while the 40-kilovolt curve reached a steady state in about 9 min.

Plotting these data logarithmically (fig. 7), it is seen that they are straight lines, not quite parallel. The current for 20 kv is given by

$$i = 43t^{-0.077}.$$

This relation held for times  $T_0$  as low as 0.5 sec. It is obviously impossible from these data to compute the current for  $T_0=0$ ; and equally impossible for the current to become infinite at  $T_0=0$ .

Figure 8 shows a set of curves made under the same general conditions as those in figure 4—voltage increasing and decreasing by steps. The curve (circles) for increasing voltage are roughly parallel; likewise the curves for decreasing voltage (dots) are also roughly parallel. They appear, however, to be made up of two distinct parts, and also have a slope opposite in direction to that of the other curves. The point of intersection of the two curves for the same applied voltage may be taken as the logarithm of the time required to reach an essentially steady state. As indicated by the broken line these times appear to decrease with increasing voltage, as noted previously in connection with figure 6.

It is interesting to remark that Wikstrom<sup>20</sup> has found for solid dielectrics (not exposed to X-rays) similar exponential relationships between current and time—the exponent remaining nearly constant with changes in field strength. His explanation was based on volume polarization—an explanation which would not be satisfactory for nonpolar  $\text{CS}_2$ . Moreover, Whitehead and Marvin<sup>21</sup> have made probe measurements, which show potential gradients that would be produced by space charge localized near the electrodes. Kerr effect measurements by Moeller<sup>22</sup> corroborate Whitehead's findings, except that they show an asymmetry in the fields at the positive and negative plates.

<sup>20</sup> A. Wikstrom, Physics **6**, 86 (1935).

<sup>21</sup> J. B. Whitehead and R. H. Marvin, Trans. Am. Inst. Elec. Engrs. **49**, 649 (1930).

<sup>22</sup> R. Moeller, Phys. Z. **30**, 20 (1929).

## 3. MEASUREMENTS OF THE EFFECTIVE FIELD STRENGTH

The presence of a space charge has the effect of introducing a barrier potential within the cell, thereby reducing the average field

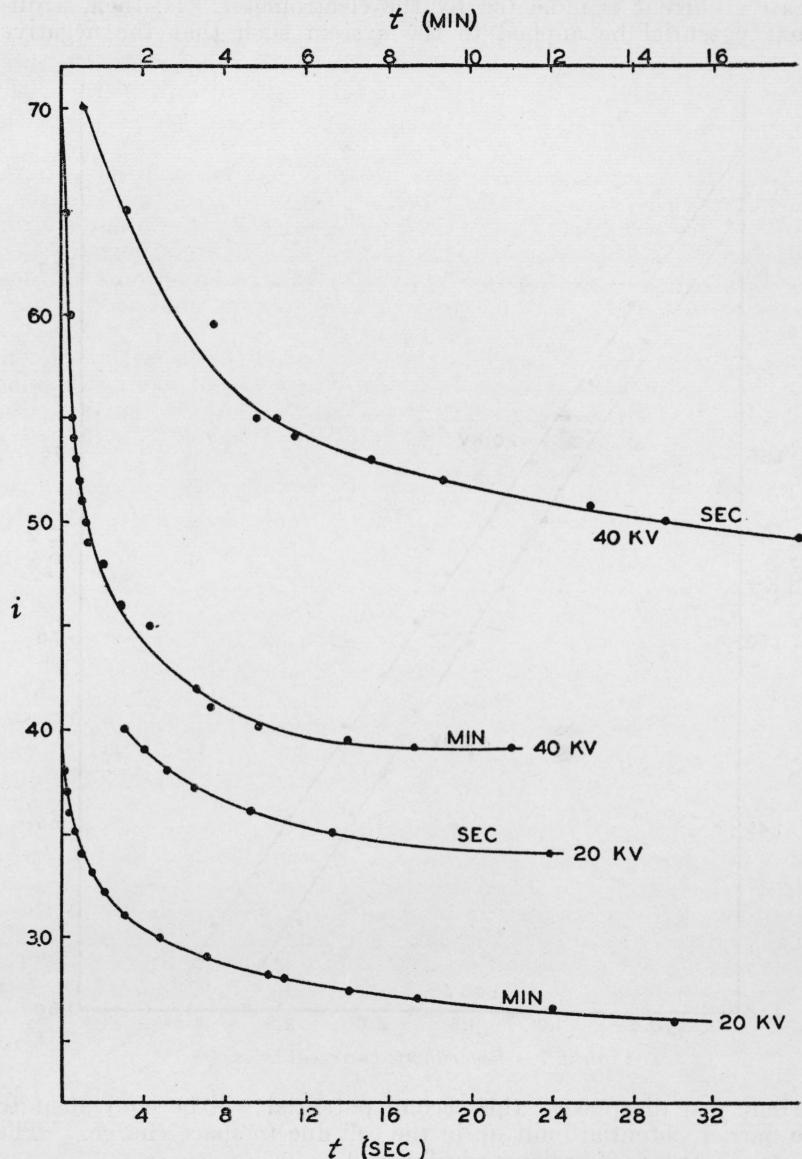


FIGURE 6.—Current-time decay curves.

strength to some value less than that to be expected from the applied voltage. Insofar as concerns the determination of the ionization at infinite field, it at least necessitates a longer extrapolation.

The magnitudes of the barrier potential were determined in a manner similar to Richardson's<sup>23</sup> method for measuring polarization. As noted above, if after an application of a potential to the cell for a certain time, it is removed and the plate earthed momentarily, a negative current is indicated by the electrometer. If, then, a different potential be applied to the system such that the negative

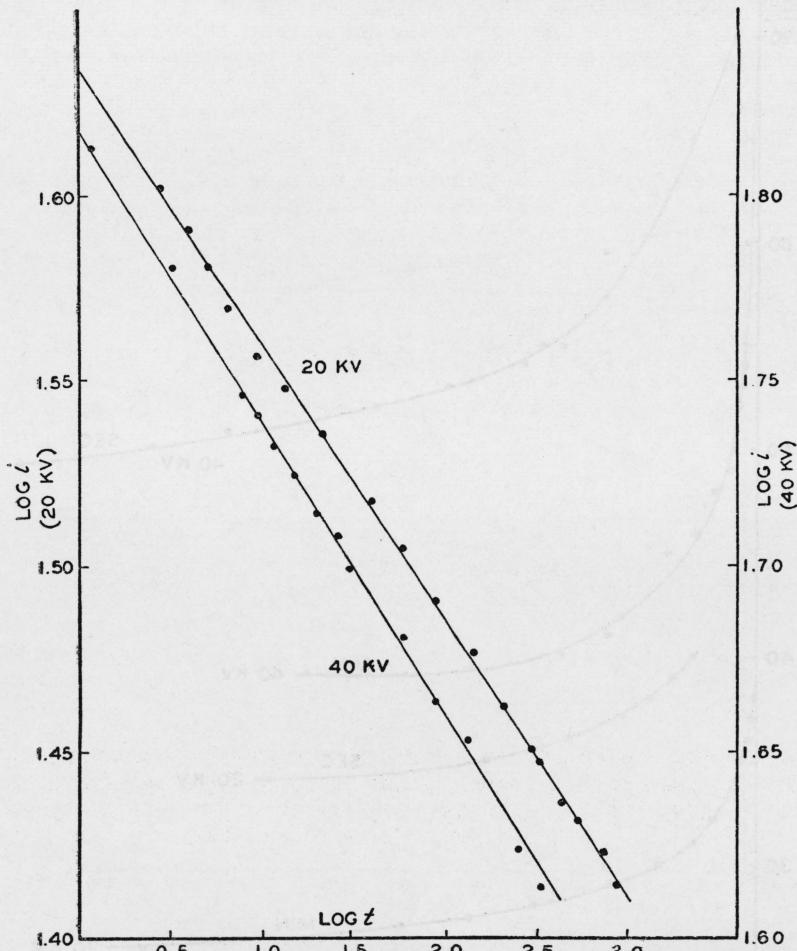


FIGURE 7.—Logarithmic current-time curves.

current just disappears, this second potential will be equivalent to the barrier potential built up in the cell due to space charge.<sup>24</sup> The electrical system is indicated in figure 9.

A hand-operated rotary switch connects the cell for any desired period with a source of potential  $+V_1$ . By swinging the arm  $S$ , as indicated by the arrow, the cell is momentarily grounded by segment  $G$ , and then connected to an adjustable potential,  $+V_2$ . Dur-

<sup>23</sup> S. W. Richardson, Proc. Roy. Soc. [A] **92**, 101 (1915).

<sup>24</sup> L. S. Taylor and F. L. Mohler, Phys. Rev. **47**, 805 (1935).

ing this time the electrometer is grounded, but at the end of the stroke the arm  $S$  depresses an insulating plunger  $P$ , which operates a multiple electrometer key, first, ungrounding the cell by opening  $a$ ; second, connecting the cell to the electrometer system by closing  $b$ ; and third, ungrounding the electrometer by opening  $c$ . This operation is repeated, each time adjusting  $V_2$ , until the electrometer shows no impulse. Reasonably consistent results are obtainable in spite of small speed variations in the hand operation of  $S$ .

Figure 10, graph  $A$ , shows the relationship between the applied potential  $V_1$  and the barrier potential  $V_2$ , in which it is seen that

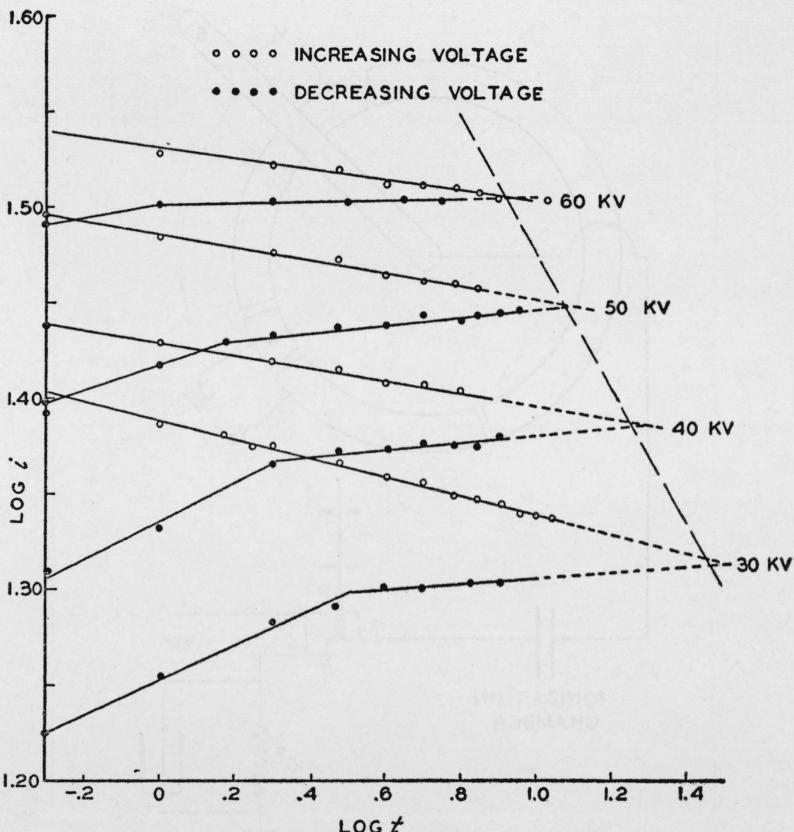


FIGURE 8.—Logarithmic current-time curves at different voltages.

$V_2$  is strictly proportioned to  $V_1$  over the whole range of potentials used. Curve 1 was taken with X-rays of moderate intensity and curve 2 with no X-rays.

Figure 10, graph  $B$ , shows the variation of  $V_2$  as a function of the radiation intensity (controlled by varying the tube current). It is seen here that the largest barrier potential is built up without exposure to radiation and that its value decreases steadily with increase in radiation intensity. This is perhaps contrary to expectations that a higher degree of ionization would produce a greater space charge. It is probably explained, however, by the fact that the increased

conductivity of the liquid permits a more rapid dissipation of space charge or ion clusters, which more than offsets the gain in charge due to a greater ionization density throughout the liquid.

#### 4. DIRECT-CURRENT "CLEAN-UP" OF LIQUIDS

With newly purified liquids there is, in addition to the decrease in conductivity due to space charge, a very much slower decrease due to electrical clean-up. In fact, such a clean-up has been applied by Nikuradse<sup>25</sup> as a phase of his purification process in the preparation

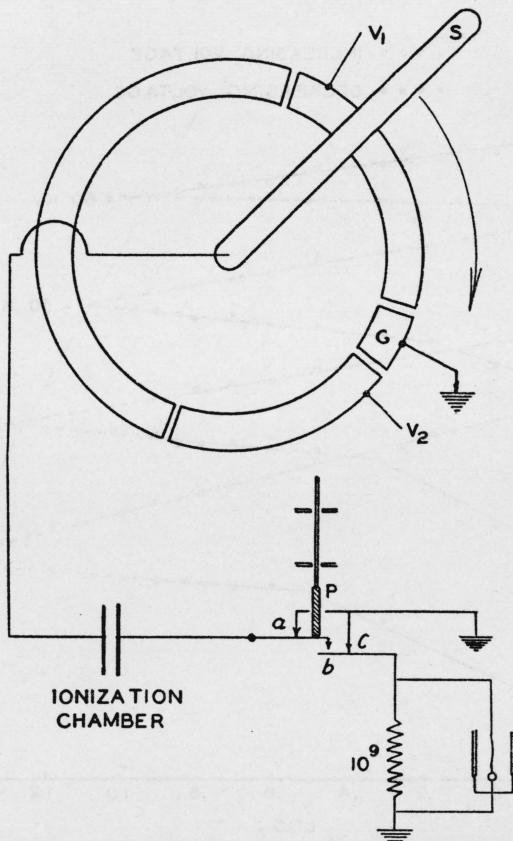


FIGURE 9.—Switching arrangement used in determination of the barrier potential.

of oils for power-factor measurements. Depending upon the type of cell and volume of liquid, electrical clean-up in our cells continued for 2 to 24 hr. Once a liquid had been so cleaned it showed relatively little recovery of conductivity.

Whitehead<sup>26</sup> in studying the current-voltage curves of transformer oils at field strengths up to 10 kv/cm reports the attainment of a saturation current. We fail to check this result with any of the liquids studied (no transformer oils). Figure 11 shows a typical current-

<sup>25</sup> A. Nikuradse, *Z. phys. Chem. [A]* **155**, 59 (1931).

<sup>26</sup> J. B. Whitehead and P. H. Marvin, *Trans. Am. Inst. Elec. Engrs.* **49**, 649 (1930).

voltage curve for  $\text{CS}_2$ , not exposed to X-rays. It is evident that while the curve is very much flatter than for the same cell when exposed to X-rays, it still shows no evidence of saturation. This particular test was carried out with  $\text{CS}_2$  which had been subjected to careful electrical clean-up.

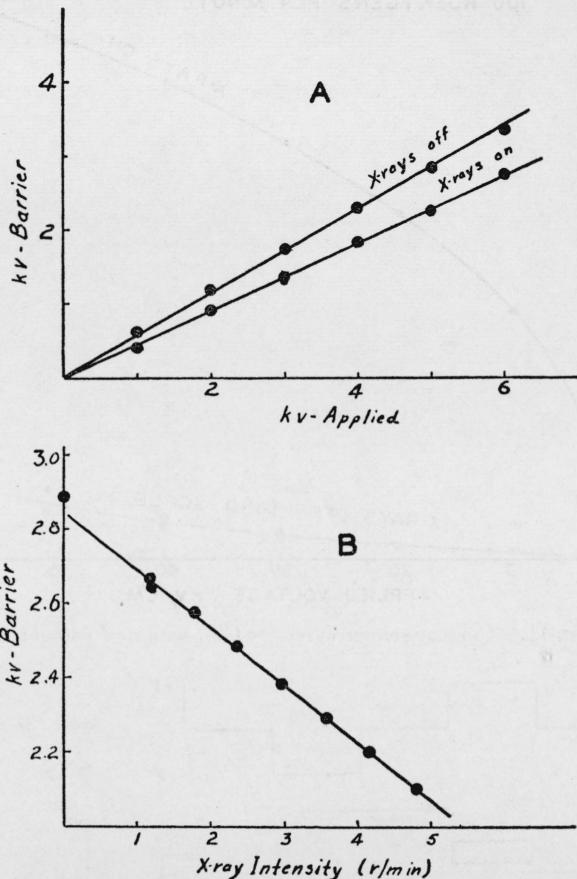


FIGURE 10.—A, barrier potential as a function of the applied potential; B, barrier potential as a function of the radiation intensity.

## VI. SHORT-PERIOD IONIZATION-CURRENT MEASUREMENTS

### 1. CURRENT-MEASURING SYSTEM

To be certain that the space charge had no effect other than to effectively decrease the average field strength in the cell, direct-current measurements of the ionization were made for values of  $T_0$  ranging as low as 0.005 sec. This gives an approach, at least, to the conditions before any space charge has been built up.

A square-wave voltage, such as indicated in figure 12, part A, was supplied to the potential electrode of the cell by means of a group of

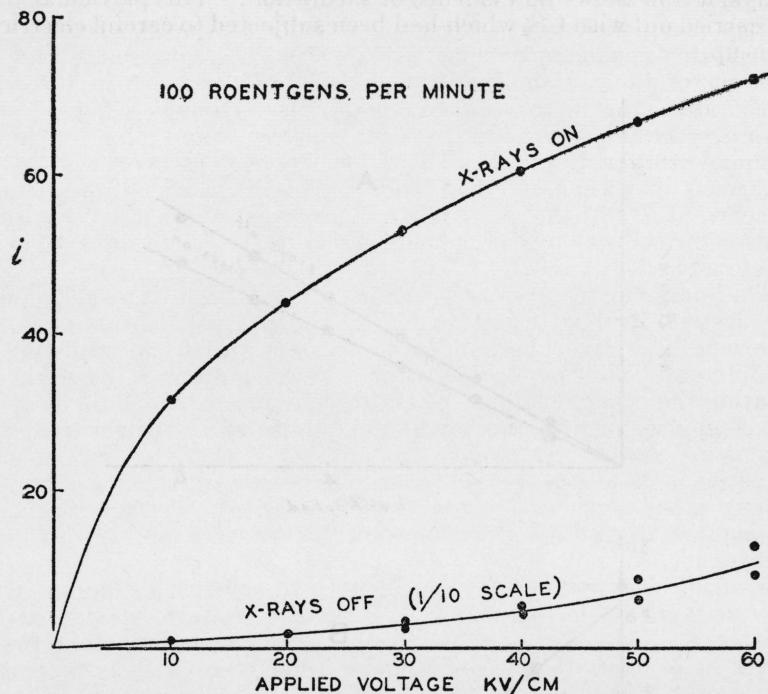


FIGURE 11.—Current-voltage curve for  $\text{CS}_2$ , with and without  $X$ -rays.

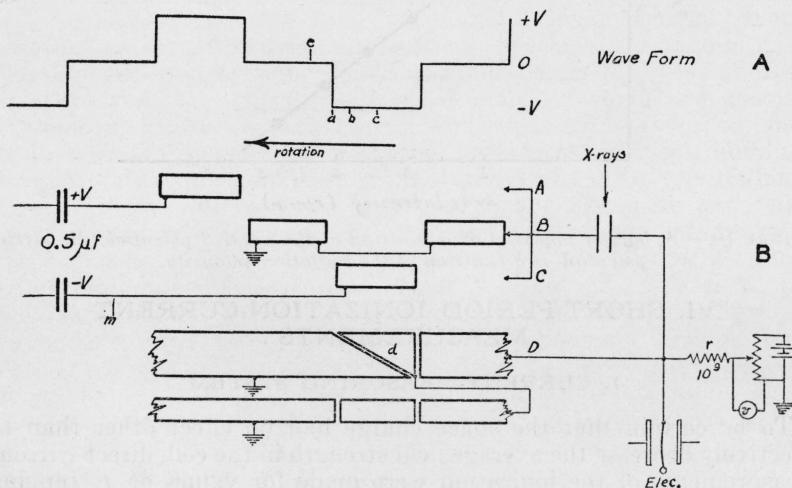


FIGURE 12.—A, square-wave voltage applied to cell; B, Commutator system for producing square-wave voltage, and current selector.

commutators operated on a single shaft and driven by a variable-speed direct-current motor. Part B of figure 12 shows the commu-

tators developed onto a plane in order to indicate the proper phase relations. Brushes *A*, *B*, and *C* are connected alternately to  $+V$ , ground, and  $-V$  through the commutators. The direct-current voltage is supplied from a kenotron rectifier having a capacitance of  $0.5 \mu f$ , this capacitance being so large in comparison with the remainder of the system that the division of voltage introduced no measurable drop in the capacitance of the rectifier. While a small drop is of no importance in itself, its recovery would induce a charge in the electrometer system. The absence of such recovery was tested by means of a moderate-frequency high-voltage string voltmeter<sup>27</sup> attached at *m*. At the same time a separate capacitance several times that of the cell was placed in the position of the cell in order to exaggerate any effect.

The electrometer system is connected to brush *D*, which keeps the system earthed, except when in contact with the segment *d*. The length of this ungrounded interval is varied by adjusting *D* at different points across the rotor. Phase position is adjusted by rotating the brush holders. The fifth commutator is for the purpose of keeping sector *d* earthed while not connected to the electrometer; this is to prevent its picking up any stray charges. By suitable adjustment it is possible to connect the electrometer to the cell at any point, such as *b*, at a time  $T_0$  after the voltage reaches a maximum value at *a*, and to maintain the connection for any interval such as *b-c*.

A string electrometer is connected to the system as shown, with a potentiometer for adjusting a balancing voltage applied across resistance *r*, which is of the order of  $10^9$  ohms. Resistance *r* also serves as a shunt to the electrometer which thus acts as a current indicator. Flexible shielded rubber cables lead to the cell, commutator, etc. The system was calibrated at the beginning and end of each run, but over a period of 18 months was found to vary only about 2 percent in sensitivity.

In making observations, the potentiometer voltage *v* was adjusted until flicker of the electrometer essentially disappeared; the ionization current was given by  $v/r$ . When the interval, *b-c*, was made too long, complete balancing of the current was not possible because the building up of space charge caused an appreciable lowering of the conductivity. In such cases one of two procedures was followed. First, the balance condition would be taken as the point where the electrometer impulse just ceased to occur in the over-balance direction. After the first few trials this point could be repeated with fair accuracy. Secondly, a neon lamp, used for illuminating the electrometer scale, was synchronized with the commutator drive shaft so as to cease glowing at a very short interval after *b*, thereby making it impossible to see the fiber except at the time of the maximum ionization current. This method simplified the balancing, but caused eye fatigue; consequently, the first method was used most of the time.

The interval  $T_0$  was set by varying either the phase position of *d* or the frequency of the applied voltage. This latter was adjustable within a range 0.01 to 30 rps and was controlled by means of a generator tachometer on the main shaft.

<sup>27</sup> L. S. Taylor, BS J. Research 5, 609 (1930) RP217.

To test for the absence of accumulated space charge, the selectors were adjusted so as to give a current reading, should such exist, at some point such as  $e$ . In no case was a measurable current observed.

## 2. CURRENT-TIME CURVES

With fixed values of  $V$  the net ionization current was measured as a function of  $T_0$ , which was varied by means of the frequency of the voltage alternations—the “dark current” being subtracted from the total in each case. Figure 13 shows a typical curve taken with a high value of  $V$  and with a fairly intense beam of radiation (about 75 roentgens per minute). The current scale is arbitrary.

The position of the break,  $b$ , appears to depend on both the applied voltage and the intensity of the radiation, qualitative measurements indicating that  $T_b$  increases with ionization density and decreases

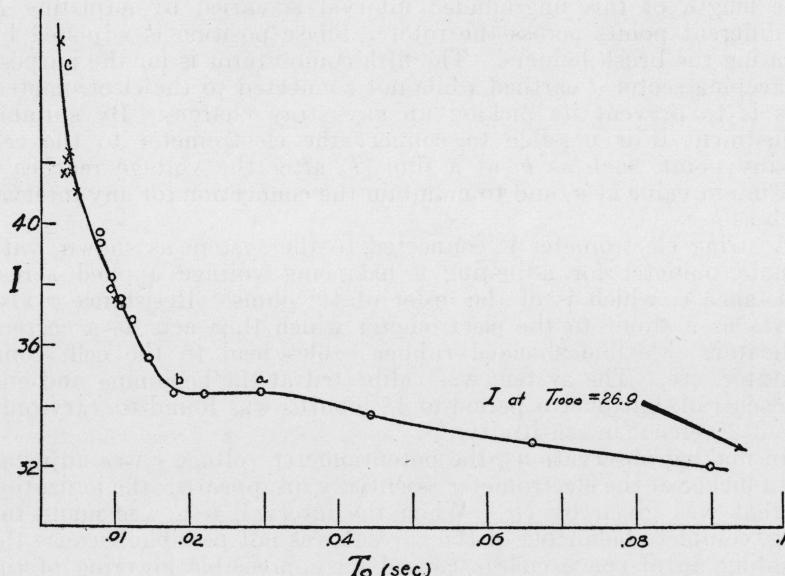


FIGURE 13.—Current-time curves for interrupted voltage.

with increase in  $V$ . It may also be noted that the value of  $I$  in the region  $ab$  is roughly what would be expected in a liquid free of space charge, on the basis of independent measurements of the barrier potential.

Throughout these experiments the liquids were exposed to X-rays almost continuously, as a consequence of which the ion density without applied voltage would be very large. Thus, when the voltage is first applied to the chamber at  $T_0=0$ , there is this large number of ions which must be swept out before the current indication gives a measure of the rate of production of new ions. The passage of these accumulated ions would account for the portion of the curve  $bc$ .

However, at the fields used here (40 to 50 kv/cm) the velocity of  $\text{CS}_2$  ions is of the order of 300 cm/s<sup>28</sup> so that the expected time neces-

<sup>28</sup>Van der Bijl, Ann. Physik 39, 170 (1912).

sary to clear the cell would be the order of 0.003 sec, whereas in all of our curves the point *b* is in the neighborhood of 0.02 sec. A number of possible explanations present themselves—perhaps the simplest of which is the effect of space charge. With the application of potential to this uniformly ionized liquid, there takes place a segregation of positive and negative ions, which, in turn, establishes a barrier potential and intensifies the very conditions we are studying. With the application of an electric field, this high ion density cannot be maintained and hence the discharge current is of a short duration. Then, at point *b* the effect due to newly produced ions becomes dominant, and extends over longer periods of time. It may well be that the two effects combine to make up the portions of the curve below *b*, although judging by the very rapid decrease in *I* between *c* and *b*, its effect probably soon becomes negligible.

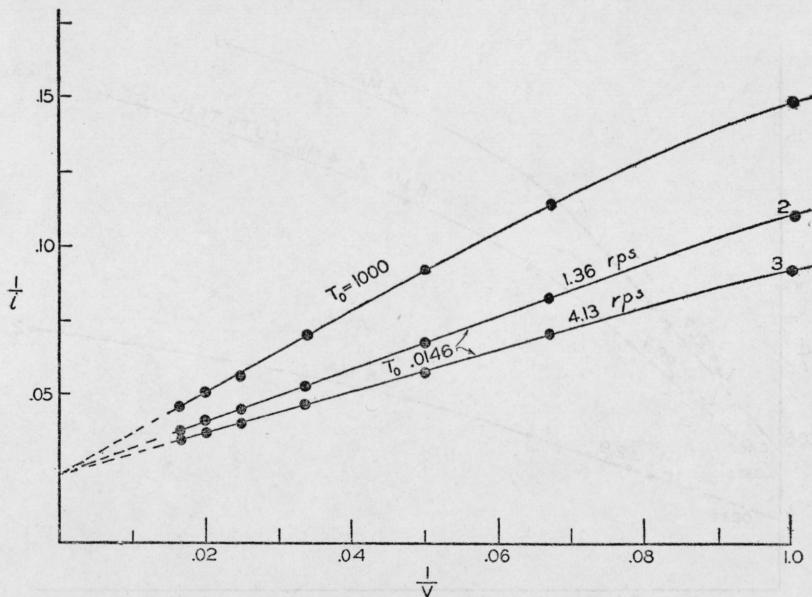


FIGURE 14.—Inverse current-voltage curves— $T_0$  varied.

An alternative explanation for the shape of this curve might depend upon the existence of heavy-ion aggregates in the field-free liquid. These, having a much lower mobility, would be cleared more slowly from the cell. The position of the break *b* would give to these ion aggregates a velocity of about 30 cm/s which is a reasonable value, corresponding to a mobility of the order of  $6 \times 10^{-4}$  cm/s/v/cm. The portions *cb* appear to be roughly of the form  $I=kt^{-2}$ , although the points are somewhat scattered.

### 3. INVERSE CURRENT-VOLTAGE CURVES

Figure 14 gives a group of curves showing the relationship between reciprocal current (arbitrary units) and reciprocal voltage for the same X-ray intensity but under different conditions of measurement. Curve 1 is for direct-current conditions ( $T_0=10$  min); curve 2, for a

square-wave voltage of 1.36 cycles/s, and curve 3 for 4.13 cycles/s; the timing selector was set for  $T_0=0.0146$  sec in both cases. It is clearly evident that all curves pass through the same point at  $1/V=0$ .

The difference in slope between the different curves is associated with the barrier potential or space charge, and it is probable that if actual average field strengths were used for abscissas in place of  $1/V$ , all the curves would coincide. This may be seen from Jaffé's equation, which is of the form  $1/I_x = C_1/X + C_2$ , so that if  $C_2$  is constant and  $1/I_\infty$  is the same, then the slope  $C_1$  must vary directly with  $1/X$ .

Thus, comparing curve 1 (full space charge) with curve 3 (no space charge) we find a slope ratio of 1:2.4, from which we may deduce, on the basis of the abscissas for curve 3 being effective field strength, that the effective field for direct-current potentials is in this case only about 42 percent of the applied field, and which is of the right order. This may be a somewhat risky conclusion since it may not

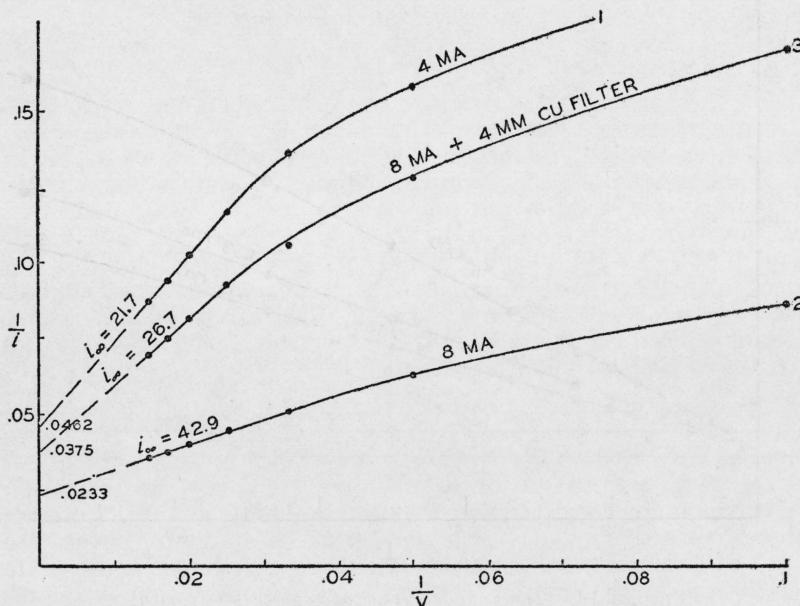


FIGURE 15.—Inverse current-voltage curves—X-ray intensity varied.

be definitely known what value of  $T_0$  should be used for zero space charge. A further complication is introduced when we note that curves 2 and 3 differ markedly in slope in spite of both having the same value of  $T_0$ , but differing in frequency. When  $T_0$  is varied while holding the frequency constant, the slopes of the curves vary in accordance with the expectations based on figure 8, all curves again passing through the same point at  $1/V=0$ .

#### 4. X-RAY-INTENSITY MEASUREMENTS

The variation of  $I_\infty$  with the intensity of the radiation is shown in figure 15, curves 1 and 2 being obtained at 160 kv (constant) with 4 and 8 ma, respectively. The values of  $I_\infty$  obtained by extrapolation are 21.7 and 42.9, being within experimental limits in the ratio of 1:2.

The proportionality of  $I_\infty$  to intensity has been found to hold within a range of at least 20:1 for a given quality of radiation.

When the quality of the radiation is changed at the same time as the intensity, the proportionality of  $I_\infty$  and intensity as measured by air ionization no longer holds. Curve 3, for 8-milliampere and 0.4-millimeter copper filtration, gives a value for  $I_\infty = 26.7$ , making a ratio of 2.13 with the value of  $I_\infty$  at no filtration. This compares with a similar ratio of 1.61 obtained by air-ionization measurements with a calibrated thimble ionization chamber.

It may be pointed out that when comparing X-ray intensities of a given quality by means of a liquid ionization chamber, single measurements made at a given chamber potential may be used, provided they fall on the straight portions of the curves. Potentials corresponding to the curved portion of the plots can only rarely be used in intensity comparison. With direct current applied fields in excess of 25 kv/cm must, in general, be used, while with the square-wave voltage, field strengths as low as 10 kv/cm may sometimes be used.

### 5. ALTERNATING-CURRENT CLEAN-UP

It may be noted, that contrary to the fact that liquids are subject to direct-current clean-up, there is little or no evidence of alternating-current clean-up. As the liquid in a chamber ages over a period of several weeks, the leakage current produced by a pulsating voltage may grow steadily larger, but not always. On the other hand, the ionization current due to X-rays does not change to a measurable extent during this time. This would indicate that the liquid is not subject to an effective chemical change, other than to a small amount of electrolytic dissociation; in the case of  $\text{CS}_2$  some sulphur separates out from exposure to sunlight. The important fact is that the net effect due to radiation is not changed.

### 6. EFFECTIVE VOLUME OF IONIZATION CHAMBER

Since it is desired to use the grid type of electrode in subsequent work, a study was made of the effective volume of an ionization chamber having grid electrodes. Aluminum wires about 0.1 mm in diameter were strung about 0.9 mm apart on aluminum rings (see fig. 3) two of which were placed on both faces of a fused-quartz plate about 70 mm in diameter and having a hole about 1 cm in diameter at the center. Several such plates having thicknesses ( $d$ ) of 0.5, 1.0, 1.5, 2.0, and 2.5 mm were used. The electrodes were so shielded as to prevent any ionization reaching the measuring electrode except from the volume occupied by the hole in the quartz plate.

Reciprocal plots of the ionization current were obtained for different volumes, under the same X-ray conditions, from which saturation currents,  $I_\infty$  given in table 1, were obtained by extrapolation.

TABLE 1

Cell thickness ( $d$ )	$1/I_\infty$	$I_\infty$	$I_\infty/d$
mm			
0.5.....	0.405	2.47	4.94
1.0.....	.205	4.88	4.88
1.5.....	.138	7.24	4.83
2.0.....	.102	9.80	4.90

$I_\infty/d$  gives a measure of the ionization per unit volume at different cell thicknesses, and it is seen that the maximum deviation from the mean is only slightly over 1 percent, which is probably less than the experimental error. Comparisons between the ionization per unit volume measured with grids and with thin (0.2 mm) aluminum plates were in fair agreement—the greatest source of uncertainty being the absorption correction necessary for the plates.

### 7. IONIZATION WITHOUT X-RAYS

As an explanation of the residual conductivity of such liquids as here used, it has been variously suggested as due to the ionization produced by cosmic radiation.<sup>29,30</sup>

However, the conductivity of the purest liquids we have been able to obtain (tetralin) has been much too large to be accounted for on such a basis. For example, the X-ray intensity used for the 8-milliampere curves in figure 15 was of the order of 100 r/m, and gave a value  $I_\infty = 42.5$ . At the same time, the dark current or residual conductivity was 0.5 at a field strength of 60 kv/cm, which would correspond to about 1.1 r/min. This, compared with a cosmic-ray intensity of the order of  $10^{-5}$  r/min makes it obvious that cosmic rays cannot have an appreciable effect upon the residual conductivity. It may be possible that a portion of the residual conductivity occurs through the body of the quartz, which has about 10 times the area between plates as the  $\text{CS}_2$ . Even assuming equal conductivities for quartz and  $\text{CS}_2$  (which is contrary to experience) there is a discrepancy of  $10^4$  between the measured and calculated cosmic-ray ionization.

### 8. UNIPOLAR CONDUCTIVITY

In a short abstract of this work<sup>31</sup> mention was made of a unipolar conductivity in  $\text{CS}_2$ . Careful subsequent measurements failed to verify this effect for either steady or fluctuating voltages—our earlier measurements evidently having been subject to some undetected error. On the other hand, several observers have reported a unipolar conductivity.<sup>32</sup> It is probable that their findings are influenced by asymmetrical field conditions introduced through the use of cylindrical electrodes,<sup>33,34</sup> or point to plate electrodes.

WASHINGTON, July 2, 1936.

<sup>29</sup> G. Jaffé, Ann. Physik **25**, 257 (1908).

<sup>30</sup> See review article by A. Nikuradse, Phys. Z. **33**, 551 (1932).

<sup>31</sup> L. S. Taylor, Phys. Rev. **49**, 860 (1936).

<sup>32</sup> A. Nikuradse, Arch. Elektrotech. **22**, 305 (1929); **26**, 362 (1932).

<sup>33</sup> G. Jaffé, Ann. Physik **23**, 326 (1909).

<sup>34</sup> H. Ealer and C. A. Knorr, Z. physik. Chem. [A] (1932).